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Anomalous Isotope Shift of a Phonon Mode Coupled to a Tunnelling System.

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Abstract. - It is demonstrated that a harmonic oscillator coupled to a tunnelling system can only exhibit negative frequency shifts if the coupling strength is allowed to depend on the tunnelling frequency. The results can be used to understand the anomalous isotope shifts observed in far infra-red and Raman spectra of the tunnelling off-centre Li^+ impurities in KCl.

The frequencies of a linearly coupled spin-phonon system have been calculated for the whole range of physically meaningful values of the coupling strength. The motivation for this originated in the intriguing problem of long standing concerning the anomalous $^7\text{Li} \rightarrow ^6\text{Li}$ isotope shift of the 43 cm^{-1} mode observed both in far infra-red (IR) absorption and Raman scattering of the off-centre Li^+ impurity in KCl [1, 2]. This $\langle 111 \rangle$ displaced substitutional Li^+ ion is archetypal of a whole class of off-centre atomic and molecular ions exhibiting tunnelling motions between equivalent positions in ionic crystals. In KCl the tunnel splitting corresponding to the tunnelling motion of the most abundant ^7Li isotope (93%) between the eight $\langle 111 \rangle$ off-centre positions is 0.82 cm^{-1} , which increases to 1.15 cm^{-1} for ^6Li (7%) [3-5]. This positive isotope shift contrasts with the 43 cm^{-1} Raman-mode which exhibits an anomalous decrease of about 1 cm^{-1} when the $^7\text{Li} \rightarrow ^6\text{Li}$ substitution is made [1, 2]. As discussed in subsect. IV.C of ref. [6], the simultaneous Raman- and IR-activity of this resonance is a consequence of the off-centre relaxation, resulting in a breakdown of the parity of the full cubic group O_h .

In spite of several efforts, this negative-isotope effect has not yet received a satisfactory or convincing explanation essentially for two reasons: i) because of its IR activity, the 43 cm^{-1} mode has been initially but erroneously ascribed to a motion of Li^+ [1, 7], and ii) in modelling the KCl: Li^+ system, investigators have focussed on fitting the experimental parameters to a *static* multiwell off-centre potential. For example, in the work of Devaty and Sievers [8], the isotope effect of the tunnelling transitions within the ground-state multiplet and its evolution under increasing hydrostatic pressure is fitted to a three-dimensional static potential, which was taken to be separable into three one-dimensional

double-well contributions. However, as also stated by the authors, this approach does not account for the isotope effect of the 43 cm^{-1} mode.

Recently [6], it was established through an analysis of the polarized Raman spectra of the 43 cm^{-1} mode that it belongs to the A_1 representation of O_h and not to a representation of the C_{3v} group of the off-centre Li^+ centre. Therefore, this mode originates from the motion of the ions surrounding the Li^+ impurity rather than from a vibration of the Li^+ itself. A similar interpretation applies to the low-frequency mode of the F_A (Li^+) centre in KCl [9]. Our conclusions are in accord with an earlier calculation of the phonon density of states of a finite KCl cluster around the Li^+ ion: Sangster and Stoneham have shown that the displacements of the surrounding ions are mainly involved in the low-frequency resonance and, consequently, no Li-isotope effect should be expected for this mode [10]. In this letter it is shown that for an isotope effect to occur for this low-frequency phonon mode the *coupling* with the tunnelling is most essential, rather than the precise shape of the static off-centre potential.

The previous experimental and theoretical findings imply that the observed anomalous phonon-frequency shift originates from a different interaction of the ^6Li and ^7Li tunnelling motions with the 43 cm^{-1} phonon mode. A full microscopic description of the Li^+ impurity embedded in the host crystal is exceedingly complicated and probably not transparent. We have looked for the most simple model system that can account, at least qualitatively, for the observed features. The model Hamiltonian reads ($\hbar = 1$):

$$H = -h\sigma^x + (\Omega C)^{1/2} \sigma^z(a^\dagger + a) + \Omega a^\dagger a. \quad (1)$$

σ^x and σ^z are Pauli pseudo-spin-operators describing the tunnelling object with frequency $2h$, $a^\dagger(a)$ is the creation (annihilation) operator for the oscillator mode with energy Ω and C is the binding energy, determining the strength of the spin-phonon interaction. A linear coupling between tunnelling and phonon operators was previously used in ref. [10], where the IR transition was considered a phonon sideband on a tunnelling transition and its lineshape was calculated.

The properties of model (1) are most directly obtained by numerical diagonalization of (finite) matrices representing Hamiltonian (1). To this end, a state of the system is expressed as a linear combination of direct products of the L lowest oscillator eigenstates and the eigenstates of σ^z . A straightforward calculation then yields a $2L \times 2L$ matrix, approximating the infinite matrix (1). The eigenvalues and eigenstates obtained from diagonalizing this $2L \times 2L$ matrix approximate the $2L$ lowest eigenvalues and eigenstates of (1) [11]. In practice we have found that four-digit accuracy for the 8 lowest eigenvalues could be achieved with $L \leq 64$, for the whole range of physically meaningful values of h , Ω and C . Similar ideas have already been employed to study the ground-state properties of an exciton-phonon system [12]. In the present letter the knowledge of the low-lying states is exploited to investigate the time-dependent properties.

The dominant contributions to the zero-temperature phonon spectrum are obtained by Fourier transformation of the time-dependent phonon-correlation function

$$\langle x(t) x(0) \rangle = \sum_{j=0}^{2L-1} \exp[i(E_j - E_0)t] |\langle \psi_0 | x | \psi_j \rangle|^2, \quad (2)$$

where $x = (a + a^\dagger)/\sqrt{2\Omega}$ and E_i and ψ_i are the eigenvalues and eigenstates of Hamiltonian (1). The contribution in this spectrum with peak position near Ω is to be identified with the effective frequency $\tilde{\Omega}$ of the oscillator motion. For increasing coupling C this contribution gets less weight in favour of a sideband transition near the tunnelling-frequency $2h$.

According to the experimental data on the Li^+ defects, we consider the regime $\Omega \gg 2h$. The other regime $\Omega \leq 2h$ was found to behave differently and will not be discussed here. In fig. 1, we plot $\tilde{\Omega}$ as a function of the coupling parameter C for three different values of the tunnelling frequency $h_1 < h_2 < h_3$ and with Ω fixed. It is seen that $\tilde{\Omega}$ starts from Ω at zero-coupling, goes through a maximum at $C = \Omega/2$ and then falls off rather slowly for increasing C . The curves can be represented within an error of 1% by the function $\tilde{\Omega}(C) \equiv \Omega + aC \exp[-2C/\Omega]$, where a is determined from the value of $\tilde{\Omega}$ at $C = \Omega/2$. In a completely analogous way, the effective tunnelling frequency $2\tilde{h}$ can be determined from the spin correlation function $\langle \sigma^z(t) \sigma^z(0) \rangle$. The results for \tilde{h} are presented in fig. 2 for the same bare tunnelling frequencies h_1, h_2, h_3 and the same value Ω as in fig. 1. In contrast to $\tilde{\Omega}$, \tilde{h} decreases monotonically with the spin-phonon coupling C and fits extremely well [12] to $\tilde{h}(C) \equiv h \exp[-C/b]$, where b is an adjustable parameter.

We will now demonstrate that these results can be combined in such a way as to provide a possible unified explanation for the observed (negative and positive) isotope phonon-shift. The free motion of the defect is thought to be represented by the two-level system, *i.e.* the first term in (1). Considering two isotopes with masses $m < M$, we may (without losing generality) make the very plausible assumption that the bare tunnelling frequency slows down with increasing isotope mass, hence $h_m > h_M$. In the following, m and M will be used as subscripts to distinguish between the two isotopes. Without loss of generality we can let h_M correspond to h_1 in fig. 1, 2 and h_2 (or h_3) to h_m .

In order to get a negative isotope phonon-shift $\tilde{\Omega}_m < \tilde{\Omega}_M$ it is clear from fig. 1 that one has to make the coupling parameter « C » mass-dependent, thus $C_m \neq C_M$. The physical plausibility of this assumption will be discussed later. From fig. 1, it follows directly that a chosen pair (C_M, C_m) will either result in positive- or negative-isotope shift. This is most conveniently visualized in the (C_M, C_m) -plane as illustrated in fig. 3a). One sees that there are different regions, the precise location of the separatrices depending on the actual value of h_m used (choosing other values of h_m does not change the qualitative features of the

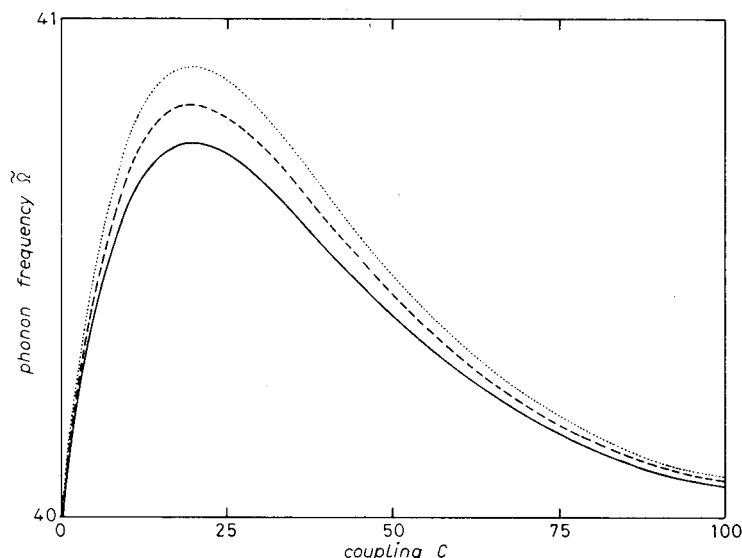


Fig. 1. – Effective phonon frequency $\tilde{\Omega}$ as a function of the coupling parameter C for a fixed oscillator frequency $\Omega = 40$. The three curves are drawn for different values of the bare tunnelling frequency h_1, h_2 and h_3 . It is seen that for increasing C , $\tilde{\Omega}$ starts at Ω , goes through a maximum at $C = \Omega/2$ and then decreases again. — $h_1 = 1.0$, --- $h_2 = 1.1$, $h_3 = 1.2$.

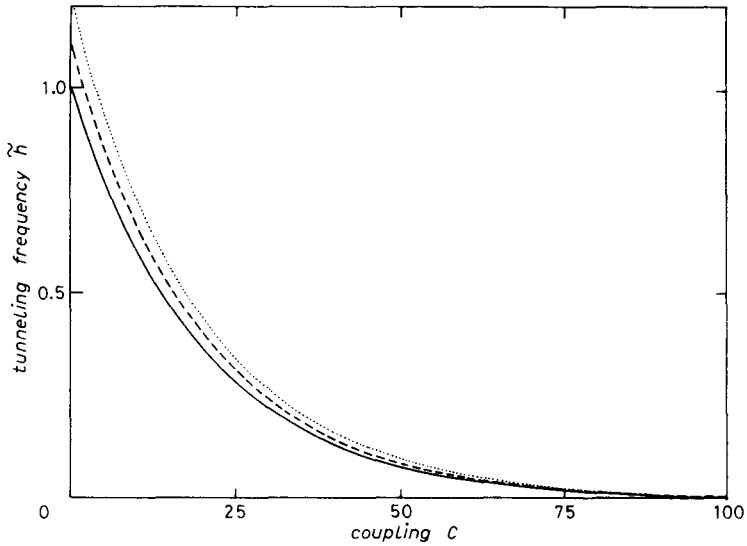


Fig. 2. – Effective tunnelling frequency $2\bar{h}$ as a function of the coupling parameter C for a fixed oscillator frequency $\Omega = 40$. The three curves are drawn for different values of the bare tunnelling frequency h_1 , h_2 and h_3 . — $h_1 = 1.0$, --- $h_2 = 1.1$, $h_3 = 1.2$. \bar{h} starts at h at zero-coupling and decreases exponentially for increasing coupling.

curves). In the limiting case $h_m = h_M = h_1$, there is no isotope effect and evidently $C_m = C_M$. In going from h_1 to h_2 and further to h_3 , the isotope effect increases and it is seen that the region of negative shift shrinks. Note that one can have negative-isotope shift above, as well as below the diagonal $C_m = C_M$, leaving the question whether $C_m < C_M$ or $C_m > C_M$. If one additionally assumes $|C_m - C_M| \approx 0$ (i.e. stay close to the diagonal), $C_m < C_M$ implies a «weak» coupling, while $C_m > C_M$ implies a «strong» coupling, both with respect to $C = \Omega/2$.

To rule out either $C_m < C_M$ or $C_m > C_M$, one has to combine the results obtained above with the analysis of the isotope effect on the tunnel frequency. Starting from fig. 2 and proceeding in exactly the same way as above, a new division of the (C_M, C_m) -plane in regions of positive and negative tunnelling frequency shifts can be made, as shown in fig. 3b). Assuming a positive tunnelling frequency shift upon isotope substitution, the (C_M, C_m) -

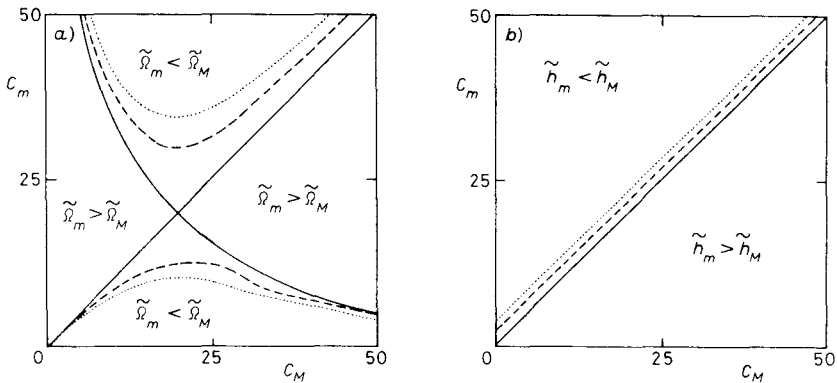


Fig. 3. – Regions of negative ($\tilde{\Omega}_m < \tilde{\Omega}_M$) or positive ($\tilde{\Omega}_m > \tilde{\Omega}_M$) phonon-frequency shift (a)), and regions of negative ($\tilde{h}_m < \tilde{h}_M$) or positive ($\tilde{h}_m > \tilde{h}_M$) tunnelling frequency shift (b)). In both figures h_M is fixed at h_1 , $h_m = h_1$ (full line), $h_m = h_2$ (dashed line), $h_m = h_3$ (dotted line) and $\Omega = 40$.

values are restricted to the region under the diagonal and only a very small area above it. Comparison of fig. 3a) and b) shows that the region above the diagonal is too small to overlap with negative phonon frequency shift regime. We, therefore, conclude that negative phonon frequency shift and positive tunnelling shift can only be found in the region $C_m < C_M$.

To investigate whether or not one can actually have the spin-phonon coupling-strength C depending on the mass of the tunnelling object, one has to examine a model more complicated than (1). Consider the Hamiltonian ($\hbar = 1$)

$$\mathcal{H} = \frac{p^2}{2m} + U(x^2 - 1)^2 + \Omega^{1/2}(\alpha x^3 + \beta x)(a^\dagger + a) + \Omega a^\dagger a, \quad (3)$$

describing the motion of a particle with mass m in a perturbed double-well potential, α and β determining the nature of the distortion. For sufficiently deep off-centre wells it has been shown [13] that model (3) can be approximated by spin-phonon system (1), thereby establishing the correspondence between the parameters entering (3) and \hbar and C . We choose a potential well with harmonic barriers, making it straightforward to determine the precise dependencies analytically and found that for increasing mass m , \hbar decreases monotonously, while

$$C = (c\beta(m)^{-1/2} + \beta + \alpha)^2, \quad (4)$$

with c a positive constant. We have verified that for relevant values of m , one can have either $\partial C/\partial m > 0$ or $\partial C/\partial m < 0$, depending on α and β . The condition $\partial C/\partial m < 0$, required for a negative phonon frequency shift in combination with a positive tunnelling frequency shift, is met when $-\alpha < \beta < 0 < \alpha$ and when $\alpha < 0 < \beta < -\alpha$. These findings make it physically acceptable to assume the binding energy C in Hamiltonian (1) to be mass dependent. The precise dependence is determined by the shape of the deformation as given by α and β .

To summarize, if one assumes that the model Hamiltonian (1) applies to the low-frequency phonon mode in KCl:Li⁺, one can situate this defect system in the intersection of the regions $\tilde{\Omega}_6 < \tilde{\Omega}_7$ and $\tilde{h}_6 > \tilde{h}_7$ (fig. 3a) and b)). It can reasonably be expected that the coupling strength of Li⁺ with the lattice does not drastically change upon isotope substitution. Hence the tunnelling motion of Li⁺ must be weakly coupled to the phonon resonant mode near 43 cm⁻¹. Finally we want to point out that this conclusion is not in contradiction with the idea that in order for the Li⁺ to be localized in an off-centre potential well, the coupling of the spin with the acoustic phonons has to be strong [14]. In the present work, Hamiltonian (1) only accounts for the tunnelling motion between equivalent off-centre positions, whereas in ref. [14] the spin-phonon Hamiltonian models the transition from on-centre to off-centre position of the defect.

* * *

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